No. II. — ON α- AND β-CHLORDIBROMACRYLIC ACIDS.*

By Charles F. Mabery and Rachel Lloyd.

α-Chlordibromacrylic Acid.

In a former paper by F. C. Robinson and one of us,† a brief account was given of certain experiments in which we had tried to obtain an addition product of brompropiolic acid with chlorine monobromide. Although the results then obtained were rather unsatisfactory, it seemed possible nevertheless to prepare the addition product in a state of purity, and this became especially desirable when it was found that an acid of the same empirical composition could be formed from chlortribrompropionic acid.

In resuming the study of this reaction, it was evidently necessary to secure at the outset a combination of the halogens containing no free bromine, inasmuch as previous results had shown that a small percentage even of tribromacrylic acid could not be removed from the product by crystallization. On the other hand, an excess of chlorine was not objectionable since it had been found that this substance in the free state united much less readily with brompropiolic acid than when combined with bromine. The chlorine monobromide used to form this addition product was therefore made by saturating bromine at 0° with chlorine; and to insure complete saturation the resulting product was dissolved in chloroform and this solution saturated at 0°. Brompropiolic acid was then added gradually, taking care to keep the solution cold and the chlorine monobromide in excess. Chemical action immediately ensued, and the formation of the addition product was complete after standing half an hour. Evaporation of the chloroform left a solid residue, which was easily purified by crystallization from hot water.

This acid is sparingly soluble in cold, very soluble in hot water, more soluble in hot than in cold carbonic disulphide, and very soluble in chloroform. Its melting point is 104°. By slow evaporation it separates from a solution in carbonic disulphide in triclinic prisms. These crystals have been submitted to careful study by

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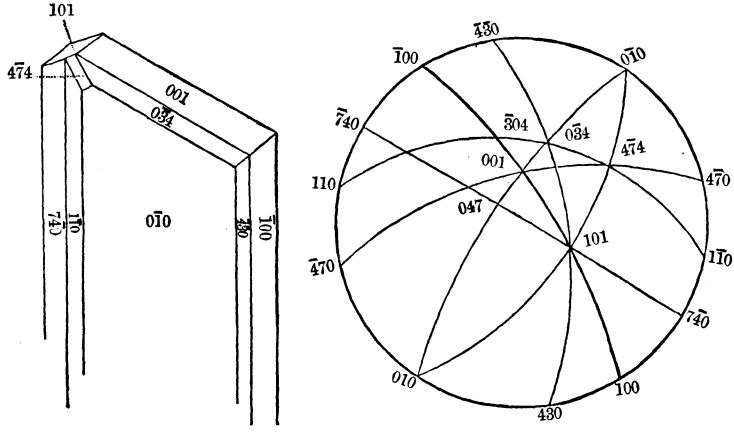
* The results described in papers II., III., and IV. were obtained under my direction in the summer course of instruction in chemistry for 1883. — C. F. M.

† These Proceedings, Vol. XVIII. p. 41.

Mr. Oliver W. Huntington,* to whom we are indebted for the following results: —

CRYSTALLINE FORM OF α-CHLORDIBROMACRYLIC ACID.



Triclinic System.

Forms {100}, {010}, {001}, {101}, {1$\bar{1}$0}, {430}, {0$\bar{3}$4}, {$\bar{3}$04}, {7$\bar{4}$0}, {$\bar{4}$70}, {4$\bar{7}$4}, {047} ?

From the fundamental angles the following values were calculated: —

X on Y 104° 43′, Y on Z 71° 6, X on Z 71° 10;

$a : b : c = 0.7981 : 1 : 0.7207.$

Angles between Normals.

	Observed.		Calculated.
010 on 100	66° 23′	Fundamental angles.	
100 " 001	116° 17′		
010 " 001	116° 20′		
100 " 101	63° 50′		
100 " 1$\bar{1}$0	47° 5′		
100 " 430			23° 52′
100 " 7$\bar{4}$0	27°		27° 5′
010 " $\bar{4}$70	42° 26′		42° 36′
00$\bar{1}$ " 0$\bar{3}$4	21°		21°

In the paper above referred to Mr. Huntington makes the following

* These Proceedings, Vol. XVIII p. 282.

remarks concerning the planes {430}, {034}, {304}, {740}, {470}, (474), {047}?: "These symbols were for the most part deduced from the zone intersections, and the indices could only in a few cases be verified by angular measurements. The faces of the vertical prism especially were very irregular, in consequence of the alternations caused by parallel grouping, so common with artificial crystals; and although the relative position of the fundamental planes could be accurately fixed, the symbols of the intermediate planes must be regarded as doubtful; these planes were seldom seen, and only in the vertical zone. The symbols given on the projection were obtained by finding the intersection with the vertical zone of other zones never well defined on the same crystal, and it can only be claimed that the approximate angular measurements on the vertical zone were compatible with the indices given above."

The composition of the purified acid was shown by analysis: —

I. 0.2254 grm. of the substance gave 0.4435 grm. AgCl + AgBr.
II. 0.2046 grm. of the substance gave 0.3980 grm. AgCl + AgBr.
III. 0.8187 grm. of the substance gave 0.3920 grm. CO_2 and 0.0273 grm. H_2O.

	Calculated for $C_3HCl_2BrO_2$.	Found. I.	II.	III.
2 Cl + Br	73.91	74.03	73.19	
C	13.56			13.05
H	.38			.37

In determining the solubility of this acid in cold water according to the method of V. Meyer, a saturated solution was neutralized with baric carbonate, and the barium determined in the filtered solution by precipitation with sulphuric acid.

I. 11.0890 grm. of a solution saturated at 20° gave 0.2344 grm. $BaSO_4$.
II. 1.6299 grm. of a solution saturated at 20° gave 0.0379 grm. $BaSO_4$.

From these results the following percentages were calculated: —

I.	II.
5.18	5.68

The barium, calcium, potassium, and silver salts of this acid were prepared and analyzed.

Baric α-Chlordibromacrylate, $Ba(C_3ClBr_2O_2)_2 . 3\,H_2O$. — On saturating an aqueous solution of the acid with baric carbonate a neutral

solution was obtained, from which, by evaporation, the barium salt separated in elongated flat prisms with oblique terminations. This salt is much less soluble in cold than in hot water. The crystals which separated from a hot solution were first dried to a constant weight in the air, then heated to 80°.

0.9545 grm. of the air-dried salt lost 0.0712 grm. H_2O at 80°.
0.8790 grm. of the anhydrous salt gave 0.3083 grm. $BaSO_4$.

	Calculated for $Ba(C_3ClBr_2O_2)_2 . 3 H_2O$.	Found.
H_2O	7.46	7.52

	Calculated for $Ba(C_3ClBr_2O_2)_2$.	
Ba	20.63	20.62

The solubility of the barium salt in cold water was also determined.

I. 1.4307 grm. of a solution saturated at 20° gave 0.1190 grm. $BaSO_4$.
II. 2.5352 grm. of a solution saturated at 20° gave 0.2142 grm. $BaSO_4$.

These results correspond to the following percentages: —

I.	II.
20.46	20.70

Calcic α-Chlordibromacrylate, $Ca(C_3ClBr_2O_2)_2 . 2\frac{1}{2} H_2O$. — The calcium salt was prepared by neutralizing an aqueous solution of the acid with calcic carbonate. From the concentrated solution the salt separated in irregular branching needles, which lost two and one half molecules of crystal water at 80°, after drying to constant weight in the air.

I. 1.2644 grm. of the air-dried salt lost 0.1006 grm. H_2O at 80°.
II. 0.9273 grm. of the air-dried salt lost 0.0714 grm. H_2O at 80°.

	Calculated for $Ca(C_3ClBr_2O_2)_2 . 2\frac{1}{2} H_2O$.	Found. I.	Found. II.
H_2O	7.80	7.95	7.70

I. 0.8166 grm. of the anhydrous salt gave on ignition with H_2SO_4 0.2016 grm. $CaSO_4$.
II. 0.8328 grm. of the anhydrous salt gave 0.1835 grm. $CaSO_4$.

	Calculated for $Ca(C_3ClBr_2O_2)_2$.	Found. I.	Found. II.
Ca	7.05	7.26	6.47

Potassic α-Chlordibromacrylate, $KC_3ClBr_2O_2$? — A solution of the acid was carefully neutralized with potassic carbonate, evaporated to a

small volume on the water bath, and finally to dryness over sulphuric acid. It formed a deliquescent amorphous crust, in which the potassium was determined after drying at 80°.

1.0508 grm. of the salt dried at 80° gave 0.3124 grm. K_2SO_4.

	Calculated for $KC_3ClBr_2O_2$.	Found.
K	12.92	13.36

Argentic α-Chlordibromacrylate, $AgC_3ClBr_2O_2$. — The silver salt was prepared by the addition of argentic nitrate to an aqueous solution of the barium salt. It separated as a curdy precipitate, which could be recrystallized from hot water without perceptible decomposition. It crystallizes in rhombic plates, and is not affected by ordinary daylight.

0.4715 grm. of the salt gave 0.1799 grm. AgCl.

	Calculated for $AgC_3ClBr_2O_2$.	Found.
Ag	29.07	28.72

β-Chlordibromacrylic Acid.

The readiness with which chlortribrompropionic acid is decomposed by alkaline hydrates has already been described,* and chlordibromethylen was identified as one of the products when the decomposition was effected with the aid of heat in a strongly alkaline solution.

A more careful study of the conditions has shown that a halogen atom may be eliminated without severing the connection of the carbon atoms. If the solution is kept cold, and a calculated amount of the alkaline hydrate — by preference baric hydrate — is added slowly, it will retain its acid reaction until the change represented by the following equation is nearly complete:

$$2C_3ClBr_3O_2H_2 + 2BaO_2H_2 = Ba(C_3ClBr_2O_2)_2 + BaBr_2 + 4H_2O.$$

The solution must then be made slightly alkaline, and kept so for twenty-four hours. On acidifying with hydrochloric acid, the resulting chlordibromacrylic acid is partially precipitated as an oil, and the remainder may be extracted from the solution with ether.

The acid is purified by crystallization from hot water, in which it is far more soluble than in cold. It is very soluble in ether and alcohol, less soluble in carbonic disulphide and chloroform. By slow evaporation from a solution in carbonic disulphide it crystallizes in oblique prisms, which melt at 99°.

* These Proceedings, Vol. XVIII. p. 45.

Several attempts were made by Mr. Huntington to determine the crystalline form of this acid in order to compare it with that of α-chlordibromacrylic acid. But unfortunately all the crystals we were able to obtain for that purpose gave very imperfect reflections, and Mr. Huntington was able to say only that in their general habit they resembled closely those he had already measured of the α-acid. A few planes gave fairly good reflections, and the angles thus measured were nearly the same as those of the α-acid.

	α-Chlordibromacrylic Acid.	β-Chlordibromacrylic Acid.	Calculated.
010 on 100	66° 23′	67°	
010 " $\bar{4}70$	42° 26′	44° 25′	
$0\bar{1}0$ " $7\bar{4}0$		42° 26′	42° 36′

The composition of the purified acid was established by analysis.

I. 0.2472 grm. of the substance gave 0.4869 grm. AgCl + AgBr.
II. 0.2060 grm. of the substance gave 0.4016 grm. AgCl + AgBr.
III. 0.7566 grm. of the substance gave 0.3690 grm. CO_2 and 0.0325 grm. H_2O.
IV. 0.4714 grm. of the substance gave 0.2319 grm. CO_2 and 0.0227 grm. H_2O.

	Calculated for $C_3HClBr_2O_2$.	Found. I.	II.	III.	IV.
Cl + 2Br	73.91	74.09	73.33		
C	13.61			13.30	13.42
H	.38			.48	.54

The solubility of the acid was determined by the method of V. Meyer. After neutralization with baric carbonate the barium was precipitated from the filtered solution with sulphuric acid.

I. 7.1822 grm. of a solution saturated at 20° gave 0.0789 grm. $BaSO_4$.
II. 5.3623 grm. of a solution saturated at 20° gave 0.0548 grm. $BaSO_4$.

From these results the following percentages were calculated: —

I.	II.
2.69	2.50

A study of the salts of this acid developed important differences between them and the corresponding salts of α-chlordibromacrylic acid.

Baric β-Chlordibromacrylate, $Ba(C_3ClB_2O_2)_2 . 3\,H_2O$. — A solution of the acid was heated with an excess of baric carbonate, filtered, and concentrated by evaporation. On cooling, the barium salt crystallized in oblique slender prisms, which were somewhat more soluble in cold water than the barium salt of the α-acid. After drying to a constant weight in the air the salt contained three molecules of crystal water, which were slowly given up over sulphuric acid, but more rapidly at 80°.

I. 0.7765 grm. of the air-dried salt lost 0.0565 grm. H_2O at 80°.
II. 1.0502 grm. of the air-dried salt lost 0.0782 grm. H_2O at 80°.
III. 0.7185 grm. of the anhydrous salt gave 0.2462 grm. $BaSO_4$.
IV. 0.5975 grm. of the anhydrous salt gave 0.2051 grm. $BaSO_4$.

	Calculated for $Ba(C_3ClBr_2O_2)_2 . 3\,H_2O$.	Found. I.	II.
H_2O	7.52	7.27	7.45

	Calculated for $Ba(C_3ClBr_2O_2)_2$.	III.	IV.
Ba	20.63	20.15	20.18

In determining the solubility of the barium salt in cold water the following results were obtained: —

I. 1.5511 grm. of a solution saturated at 20° gave 0.1413 grm $BaSO_4$.
II. 1.8345 grm. of a solution saturated at 20° gave 0.1676 grm. $BaSO_4$.

The solubility of the salt in water at 20° is therefore shown by the following percentages: —

I.	II.
25.90	26.04

Calcic β-Chlordibromacrylate, $Ca(C_3ClBr_2O_2)_2 . 4\,H_2O$. — On concentrating a solution of the calcium salt prepared by neutralizing a solution of the acid with calcic carbonate, the salt separated in clusters of branching needles, which were less soluble in water than the calcium salt of the α-acid.

I. 1.2644 grm. of the air-dried salt lost 0.1345 grm. H_2O at 80°.
II. 0.9273 grm. of the air-dried salt lost 0.1038 grm. H_2O at 80°.
III. 1.2124 grm. of the air-dried salt lost 0.1328 grm. H_2O at 80°.
IV. 0.8820 grm. of the anhydrous salt gave 0.1887 grm. $CaSO_4$.

	Calculated for $Ca(C_3ClBr_2O_2)_2 . 4 H_2O$.	Found. I.	II.	III.
H_2O	11.27	10.64	11.19	10.91

	Calculated for $Ca(C_3ClBr_2O_2)_2$.	Found.
Ca	7.05	6.75

Potassic β-Chlordibromacrylate, $KC_3ClBr_2O_2$? — When a solution of the acid was neutralized with potassic carbonate, concentrated on the water bath, and evaporated to dryness over sulphuric acid, the potassium salt was left in the form of a very deliquescent amorphous mass. For analysis the salt was finally dried at 80°.

1.0509 grm. of the salt gave 0.4397 grm. K_2SO_4.

	Calculated for $KC_3ClBr_2O_2$.	Found.
K	12.92	12.42

All attempts to prepare a silver salt of this acid were unsuccessful. On the addition of argentic nitrate to a solution of the acid or any of its salts, the solution immediately became turbid from the separation of argentic bromide. This decomposition was not prevented to any appreciable extent by the exclusion of light.

Constitution of α- and β-Chlordibromacrylic Acids.

The essential points of difference in the physical properties of these acids, which appear in their general behavior and solubility in water, as well as in their melting points, would seem to point to a difference in structure. In the degree of hydration, solubility in water and comparative stability, their salts exhibit peculiarities as marked as those of the acids themselves. Although the silver salt of the α-acid can be prepared without difficulty, the corresponding salt of the β-acid cannot be formed even with the greatest care.

While the product obtained by the action of chlorine monobromide upon brompropiolic acid may have one of two forms, —

Brompropiolic Acid.	α-Chlordibromacrylic Acid. (1.)	(2.)
CBr	CBrCl	CBr_2
‖	‖	‖
C	CBr	CCl
|	|	|
COOH	COOH	COOH

the acid resulting from the abstraction of the elements of hydrobromic acid from chlortribrompropionic acid can evidently have but one: —

Chlortribrompropionic Acid.	β-Chlordibromacrylic Acid.
CBr_2Cl	CBrCl
|	||
CHBr	CBr
|	|
COOH	COOH

Since the formula of β-chlordibromacrylic acid is identical with (1), the structure of the α-acid is probably represented by (2); or during the addition of chlorine monobromide to brompropiolic acid, the weaker halogen unites with the terminal carbon atom.

No. III. — ON β-DIBROMDICHLORPROPIONIC AND β-BROMDICHLORACRYLIC ACIDS.

By Charles F. Mabery and H. H. Nicholson.

β-Dibromdichlorpropionic Acid.

In a brief examination of the action of chlorine on β-dibromacrylic acid, it was found by F. C. Robinson and one of us,* that, although the acid was not affected at ordinary temperatures, an addition-product could readily be obtained by raising the temperature. Further study of this reaction shows that the most desirable results are obtained as regards time, as well as the quality and quantity of the product, if the temperature is kept near 100°. In one experiment after continuing the action for eight hours 5.9 grm. β-dibromacrylic acid gave 7.9 grm. of the crude β-dibromdichlorpropionic acid, which melted without purification above 90°, or ninety-six per cent of the amount of pure acid theoretically required.

The crude acid was easily purified by two or three crystallizations from a hot solution in carbonic disulphide, which deposited the greater part of the acid when cooled to 0°. It is but sparingly soluble in water, more soluble in hot than in cold chloroform, and very soluble in ether and alcohol. It crystallizes in oblique prisms, which melt at 100° and sublime slowly at higher temperatures. The composition of this acid was determined by the following analyses: —

I. 0.2142 grm. of the substance gave 0.4712 grm. AgCl + AgBr.
II. 0.8223 grm. of the substance gave 0.3485 grm. CO_2 and 0.0510 grm. H_2O.

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* These Proceedings, Vol. XVIII. p. 44.